



Spiro-(1,1')-bipyrrolidinium tetrafluoroborate salt as high voltage electrolyte for electric double layer capacitors

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HIGHLIGHTS

- The high voltage electrolyte salt SBP-BF₄ was synthesized.
- SBP-BF₄/PC and TEMA-BF₄/PC were used as electrolyte and compared.
- The highest withstand voltage for carbon/SBP-BF₄-PC system has been observed.

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ABSTRACT

A novel quaternary ammonium salt based on spiro-(1,1')-bipyrrolidinium tetrafluoroborate (SBP-BF₄) has been synthesized and dissolved in propylene carbonate (PC) with 1.5 mol L⁻¹ (M) concentration for electric double-layer capacitors (EDLCs). The physic-chemical properties and electrochemical performance of SBP-BF₄/PC electrolyte are investigated. Compared with the standard electrolyte 1.5 M TEMA-BF₄ in PC, the novel SBP-BF₄/PC electrolyte exhibited much better electrochemical performance due to its smaller cation size, lower viscosity and higher conductivity. The specific discharge capacitance of activated carbon electrode based EDLCs using SBP-BF₄/PC electrolyte is 120 F g⁻¹, the energy density and power density can reach 31 kW kg⁻¹ and 6938 W kg⁻¹, respectively, when the working voltage is 2.7 V and current density is 50 mA g⁻¹. The withstand voltage of activated carbon based EDLCs with SBP-BF₄/PC electrolyte can reach to 3.2 V, where the stable discharge capacitance and energy density are 121 F g⁻¹ and 43 Wh kg⁻¹, respectively.

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1. Introduction

Electric double layer capacitors (EDLCs), also known as supercapacitors or ultracapacitors, have received much attention recently because their excellent performance [1]. The EDLCs have higher power density and longer cycle life than secondary batteries in that the electrical charge store in the electrical double-layer formed at the electrode/electrolyte interface, which could rapidly adsorption-desorption without faradic reactions [2–5]. The EDLCs have higher energy density than traditional dielectric capacitors because the EDLCs could afford high capacitance for the high-surface-area porous carbons electrode [3,6]. Therefore, the EDLCs are widely used in smart phones, modern high-tech field of electric vehicles (EVs), hybrid vehicles (HEVs), mobile storage devices,

industrial power management and complex power systems [7–10]. However, with the expanding demand, the low energy density of EDLCs prevents them from being widely used. It is necessary to improve the energy density without sacrificing the high power density and long cycle life [11].

To the best of our knowledge, the energy density increases linearly with the capacitance and the square of voltage [1]. However, when the specific surface area of the porous carbon increases to a certain value, the mass ratio of the capacitance tends to saturate [12,13]. Furthermore, the oxygenated functional groups on porous carbon electrode surface serve as active site, which can catalyze the electrochemical oxidation, reduction of the carbon, or the decomposition of the electrolyte components [14,15]. The safe working voltage of electric double layer capacitors based on organic electrolyte (quaternary ammonium salt represented in TEMA-BF₄ electrolyte) is generally lower than 2.7 V [16–18]. Therefore, it is necessary to develop a novel electrolyte with good electrochemical stability and high working voltage (>2.7 V) to increase the energy

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density [19,20]. The PC with irritant and high flash point is chosen as solvent in this paper [21]. Meanwhile, the spiro-(1,1′)-bipyrrolidinium tetrafluoroborate (SBP-BF₄) studied in this paper is solid in room temperature (melt point about 190 °C), and has stable electrochemical performance in wide temperature range.

Recently, spiro-(1,1′)-bipyrrolidinium tetrafluoroborate (SBP-BF₄), which is a spiro-type quaternary ammonium salt, has received much attention for its excellent electrochemical properties. The molecular structure of SBP-BF₄ salt with a little symmetry characteristic ‘8’ shape, as shown in Fig. 1, and the SBP cations have a smaller volume than TEMA cations. The calculated dimensions of the SBP cations and TEMA cations are about 0.418 nm and 0.654 nm, respectively, which are in agreement with other reports [21,22]. The smaller SBP cations relative to TEMA cations can easily diffuse into the micro pore and have a higher mobility in PC than TEA-BF₄ and TEMA-BF₄, which contribute to high electrical conductivity [23,24].

K. Chiba et al. [24,25] showed that the SBP-BF₄/PC possess wide potential window, high electrical conductivity and good rate capability. The capacitance of EDLCs using SBP-BF₄/PC was larger than that of TEMA-BF₄/PC even at low temperatures –40 °C [8]. The cycle life of the EDLCs was improved using SBP-BF₄ instead of TEA-BF₄ in ethylene (EC) and ethyl acetate (EA) mixed solvents with an operating voltage of 2.3 V [21,26]. It was demonstrated that SBP-BF₄ has excellent electrochemical properties in different solvents by evaluating capacitance, temperature range and cyclability. However, there are few papers focused on the high operating voltage to increase the energy density of EDLCs. K. Naoi [20] reported the SBP-BF₄ as a high-voltage electrolyte for its high solubility in PC and dimethylcarbonate (DMC) mixture solvent systems, but the withstand voltage limited below 3.0 V in acetonitrile (ACN) system or liner carbonate system because of the poor electrochemical stability of these solvents. The alkylated cyclic carbonates as solvent for SBP-BF₄ could achieve high withstand voltage [27], yet the paper studied the solvent effect of capacitance limit in thermodynamics and kinetic analysis, and did not use other measurements to illuminate the effect of electrolyte structure.

The aim of this paper is to evaluate the properties of SBP-BF₄/PC as high voltage electrolyte for EDLCs, in view to improve the electrochemical performance in high working voltage application without compromising capacitance. In this work, firstly, the electrolyte salt SBP-BF₄ was synthesized. Then, the conductivity and the electrochemical stability windows of SBP-BF₄/PC were compared with conventional TEMA-BF₄/PC as standard electrolyte. Finally, the

capacitance, withstand voltage, energy density and power density of the capacitor were investigated and calculated to obtain the best performance parameters.

2. Experimental

2.1. Materials

The electrolyte salt SBP-BF₄ used in this paper is synthesized by one-step method, which using pyrrolidine, 1, 4-dibromobutane, sodium hydroxide (NaOH), and sodium fluoroborate (NaBF₄) in acetonitrile (ACN), followed by recrystallized from ethanol for several times. The prepared sample dried under vacuum until constant weight (yield: 90%). The PC solvent (battery grade, extra dry < 20 ppm of water) was purchased from Tianjin Jinniu power sources material Co. Ltd. (China) and used as received without further purification. The SBP-BF₄ salt was dissolved in the PC with 1.5 mol L⁻¹ (M) concentration, and then added in activated 4 Å molecular sieves to remove the tiny water. The electrolyte was prepared and placed in a glove box filled with high pure argon. The moisture content measured by Karl Fischer titration method was less than 40 ppm (Mettler–Toledo C30, Switzerland).

Capacitor electrodes were prepared by mixing activated carbon (AC), carbon black (CB), carboxymethylcellulose sodium (CMC), and styrene butadiene rubber (SBR). The activated carbon used in this paper was commercial available (Korea PCT-21). The homogeneous slurry composition of AC: CB: SBR: CMC was 80:10:5:5% wt. The slurry was spread onto aluminum (Al) foil collector, and then dried in a vacuum oven at 60 °C. Subsequently, the electrodes were pressed and punched into a diameter of 18 mm sheet with thickness of 75 μm (including 20 μm aluminum (Al) foil collector). The average mass of electrodes were about 5 mg and the activated carbon loading is about 1.57 mg per cm⁻².

2.2. Measurements

Electrical conductivity of the electrolyte was measured at 20 °C using a conductivity meter (Mettler–Toledo S30, Switzerland). The potential window was measured by an open three-electrode cell system with a glass carbon working electrode, Pt counter electrode and Ag/Ag⁺ reference electrode at room temperature in glove box. The test was measured by cyclic voltammetry (CV) at the scan rates of 5 mV s⁻¹. The reduction and oxidation potentials were defined as the potential where the limiting current density reached 0.1 mA cm⁻² [28].

The EIS (Zahner Zennium, Germany) plots were tested on full cells in the frequency range from 100 kHz to 0.001 Hz with an ac perturbation of 5 mV. The CV curves for EDLCs were tested on full cells at various scan rates (1, 10, 100, 200 mV s⁻¹). The CV curves with different voltage ranges were performed at scan rate of 1 mV s⁻¹, while the voltage ranges were from 0–2.5 V to 0–3.5 V. Galvanostatic charge/discharge (Arbin USA) tests for rate property were performed in the constant current mode at current density from 50 mA g⁻¹ to 10 A g⁻¹, while the cut-off voltage was set at 2.7 V. The galvanostatic charge/discharge tests under various charging voltages were carried out at current density about 100 mA g⁻¹ in the same cell, and the voltages ranges were from 0–2.5 V to 0–3.7 V. The gravity specific capacitance calculated from the equation $C_m = 4I\Delta t/m\Delta V$, where I is the discharge current, Δt is the discharge time, ΔV is the voltage window from the end of the ohmic drop to the end of the discharge process, and m is the active material mass of single electrode. The energy density calculate from the formula $E = 1/2CV^2$, where the C is the specific discharge capacitance of the capacitors, the V is the charge cut-off voltage. The power density calculate from the formula $P = I\Delta V/2m$, where I is the discharge current, the ΔV is the voltage window from the end

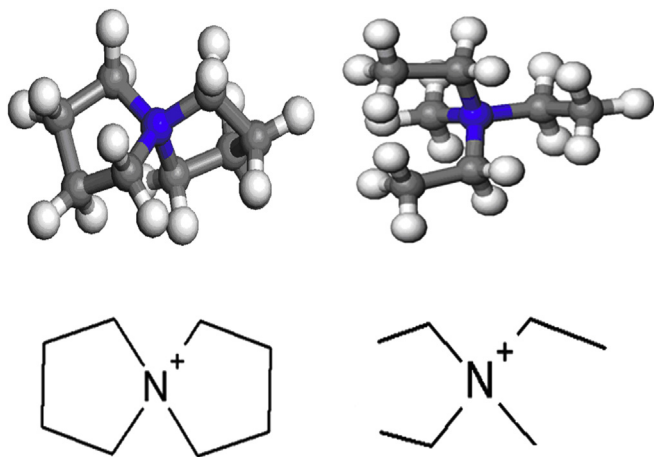


Fig. 1. Molecular structure of SBP cations and TEMA cations, white ball is H, gray ball is C, blue ball is N. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

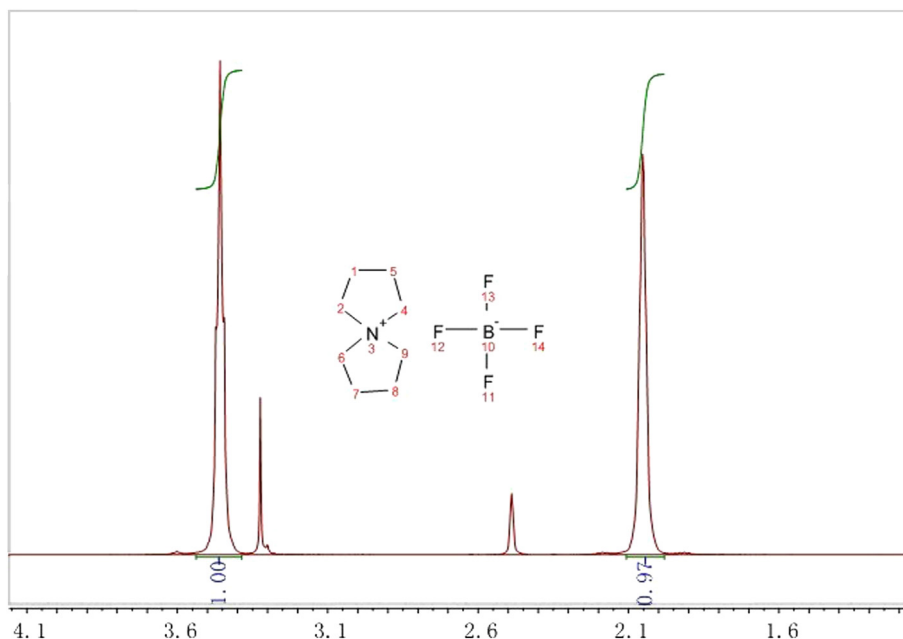


Fig. 2. The ^1H NMR spectra of the synthesized sample.

of the ohmic drop to the end of the discharge process, and the m is activated carbon material of the single electrode.

3. Results and discussion

3.1. Chemical structure and physical properties characterization of synthesized sample

The synthesized sample is dissolved in deuterated dimethyl sulfoxide ($\text{DMSO}-d_6$) for NMR characterization. Fig. 2 shows the ^1H NMR (500 MHz, $(\text{CD}_3)_2\text{SO}$) spectrum of the sample. The integral ratio of two types protons which include $\delta \sim 3.45\text{--}3.46$ ($-\text{NCH}_2-$, 8H) and $\delta \sim 2.05\text{--}2.06$ ($-\text{CH}_2\text{CH}_2\text{CH}_2-$, 8H) are approximately 1:1. The NMR data confirm that the sample is spiro-(1,1')-bipyrrolidinium (SBP), which is in agreement with the literature [29]. The $\delta \sim 2.5$ and $\delta \sim 3.3$ clearly indicate the presence of the DMSO solvent and the residual water, respectively.

Fig. 3 shows the mass spectrometry of the synthesized sample. As can be seen, the mass to charge ratio $m/z = 126.6$ which is

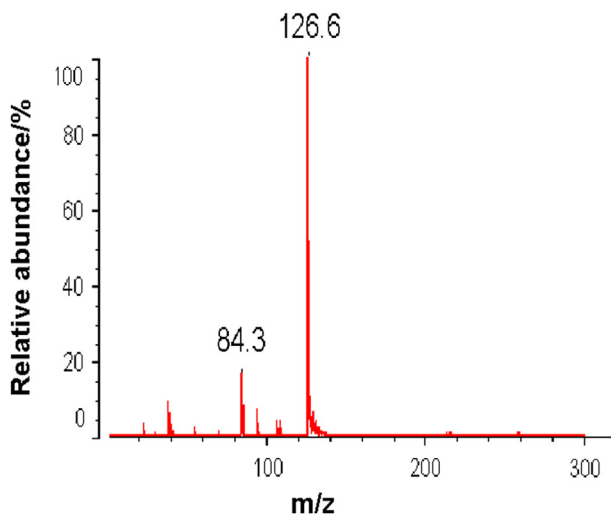


Fig. 3. The mass spectrometry of the synthesized sample.

consistent with the molecular weight of the SBP- BF_4 cationic (126.1), further confirm that the sample is SBP- BF_4 . The mass to charge ratio $m/z = 84.3$ is characteristic fragment ions amines and the structure is $\text{CH}_2=\text{CH}-\text{CH}_2-$.

The value of electrical conductivity and viscosity measured using 1.5 M SBP- BF_4 and TEMA- BF_4 in PC show in Table 1. SBP- BF_4/PC has lower viscosity than MTEA- BF_4/PC indicating that the SBP- BF_4/PC solution has better mobility. At the same concentration, SBP- BF_4/PC has higher specific conductivity than TEMA- BF_4/PC , because SBP $^+$ cations have smaller volume and higher mobility than TEMA $^+$ cations in electrolyte [24].

3.2. Electrochemical stability of SBP- BF_4/PC electrolyte

The electrochemical stability was investigated by cyclic voltammetry (CV) on different electrolyte systems. Typical polarization curves are shown in Fig. 4. Two kinds of electrolyte display wide potential window and excellent electrochemical stability. The reduction potential is limited by the decomposition of BF_4^- , and oxidation potential appeared to be limited by the decomposition of both TEMA $^+$ cations and SBP $^+$ cations. The potential windows of different electrolyte systems are almost reach to 5.2 V when the cut-off current density is $j = \pm 0.1 \text{ mA cm}^{-2}$. However, the potential window of 1.5 M SBP- BF_4/PC is a slight wider than 1.5 M TEMA- BF_4 due to high electrical conductivity of the SBP- BF_4/PC . The wider potential window of SBP- BF_4/PC can provide wide-range application for supercapacitors.

3.3. Electrochemical study in EDLCs configuration

The CV curves for EDLCs based on the 1.5 M SBP- BF_4/PC and TEMA- BF_4/PC at different scan rates are presented in Fig. 5. The rectangular shape of the CV curves at low scan rates (Fig. 5a, b)

Table 1
Conductivity and viscosity of investigated electrolytes.

Electrolyte	Concentration (mol L^{-1})	Conductivity (mS cm^{-1})	Viscosity (mPa s)
SBP- BF_4/PC	1.5	17.0	4.0
TEMA- BF_4/PC	1.5	14.6	4.5

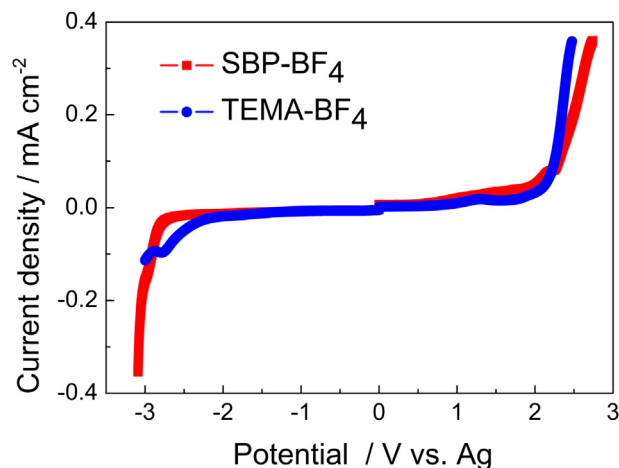


Fig. 4. Cyclic voltammograms of 1.5 M SBP-BF₄/PC and TEMA-BF₄/PC electrolyte systems measured on glass carbon working electrode, and Pt counter electrode; RE: Ag/Ag⁺; scan rate 5 mV s⁻¹; ambient temperature.

show that the capacitors based on electrolyte systems both exhibit typical double layer behavior. And the rectangular shape of CV curves both get worse as the scan rates increase. The distortion degree of SBP-BF₄/PC electrolyte based EDLCs is lower than that of TEMA-BF₄/PC electrolyte at the scan rate of 200 mV s⁻¹, which may relate with the high conductivity of SBP-BF₄/PC electrolyte. The SBP-BF₄ is more attractive for the applications in high-power type EDLCs for the SBP cations have higher mobility than that of TEMA cations at high scan rates.

Fig. 6 gives the CV curves with different voltage ranges performed at scan rate of 1 mV s⁻¹ to evaluate the electrochemical stability of SBP-BF₄ and TEMA-BF₄ in PC. There is no apparent faradic process observed in all curves even at the voltage ranges as wide as 0–3.5 V. The CV curves maintain well rectangular shape when the voltage range is from 0–2.5 V to 0–3.2 V. The distortion degree of SBP-BF₄/PC is lower than that of TEMA-BF₄/PC in the

range of 0–3.5 V, because the SBP-BF₄/PC has higher conductivity and the SBP cations have higher mobility than TEMA cations in PC. The electrolyte with high conductivity and wide electrochemical potential window could provide wide and stable work voltage range, which may play an important role in increasing the energy density of the EDLCs. The withstand voltage of the SBP-BF₄/PC electrolyte is higher than that of the TEMA-BF₄/PC electrolyte, which could enhance the working voltage and the energy density of the EDLCs.

The Nyquist spectra of SBP-BF₄/PC, TEMA-BF₄/PC based EDLCs are shown in Fig. 7a. As can be seen, the Nyquist plot includes a straight line in low frequency range representing capacitance characteristics. The 45° Warburg impedance zone in the mediate frequency range represents electrolyte ions diffusion resistance in the pores of the activated carbon. The semi-circle in the high frequency range is the contact resistance of the capacitor (including the bulk resistance and contact resistance between the particles of activated carbon). The intersection of the plot to the real axis at high frequency region is electrolyte solution resistance [18,30,31].

The capacitance of the carbon material in one electrode can be estimated by $C = 1/\pi m f Z_{im}$, where f is the frequency, Z_{im} is the imaginary part of the impedance, and m is the mass of one electrode. The capacitance vs frequency curves are shown in Fig. 7b. As can be seen, the capacitance increases rapidly with the frequency decreases in the low frequency range (< 100 Hz). In the high frequency region (> 100 Hz), capacitance values remain more stable, the two electrolyte systems give similar capacitances. This is because the deep and narrow pores cannot be penetrated by a highly alternating current [5]. In the low frequency region, the electrolyte ions penetrating into the micro pore [32,33]. The SBP ions can get into the micro pore more easily than TEMA ions since the size of the SBP ions is smaller than that of TEMA ions. The capacitance of SBP-BF₄/PC based capacitor is higher than that of TEMA-BF₄/PC based capacitor at lower frequency, which is agreement with other techniques.

The galvanostatic charge-discharge profiles of SBP-BF₄ and TEMA-BF₄ in PC electrolytes based EDLCs under various charging

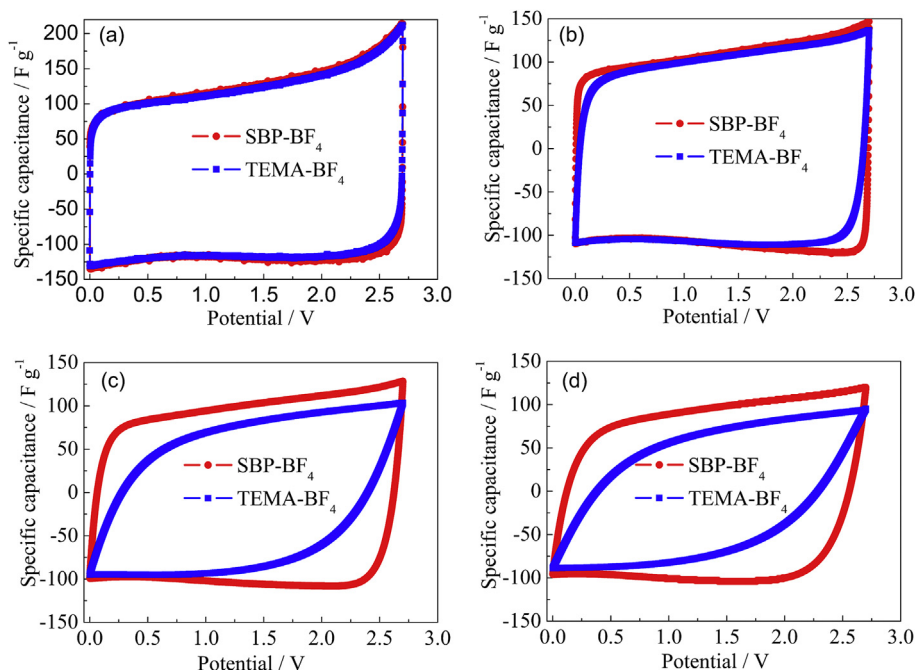


Fig. 5. CV curves of the EDLCs with 1.5 M SBP-BF₄/PC and TEMA-BF₄/PC at scan rate (a) 1 mV s⁻¹ (b) 10 mV s⁻¹ (c) 100 mV s⁻¹ (d) 200 mV s⁻¹.

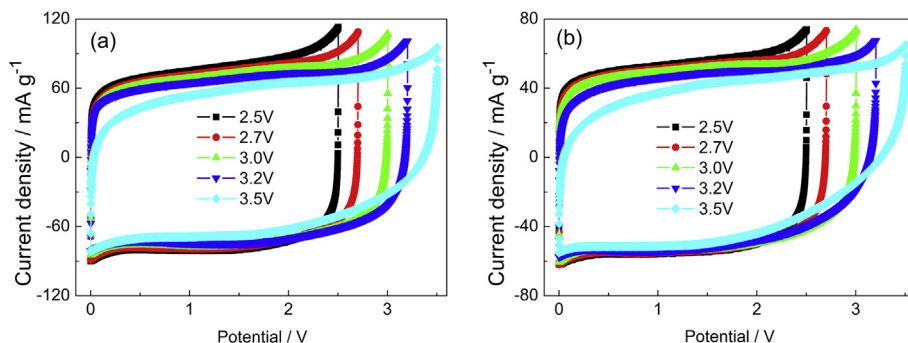


Fig. 6. CV curves of the EDLCs with 1.5 M SBP-BF₄/PC and TEMA-BF₄/PC at different voltage ranges. The scan rate is 1 mV s⁻¹. (a) SBP-BF₄/PC (b) TEMA-BF₄/PC.

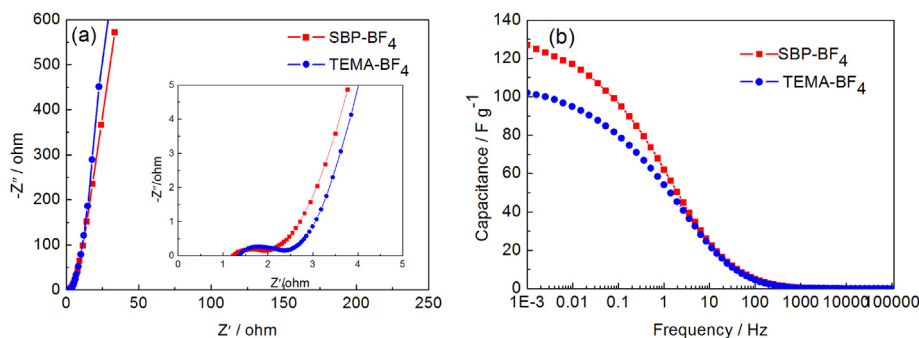


Fig. 7. (a) Nyquist plots of the EDLCs with 1.5 M SBP-BF₄/PC and TEMA-BF₄/PC. (b) Frequency response to capacitances of the EDLCs with 1.5 M SBP-BF₄/PC and TEMA-BF₄/PC.

voltages are shown in Fig. 8. When the charge–discharge voltage is less than 3.2 V, the charge–discharge curves of the SBP-BF₄/PC and TEMA-BF₄/PC electrolytes based EDLCs are linear and symmetrical showing excellent electrochemical reversibility and typical charge–discharge characteristics of EDLCs. Moreover, the sudden voltage drop (iR drop) of the discharge curves is not visible indicating that the electrode resistance is small. When the charging voltage increase to 3.5 V, the charge–discharge curves of SBP-BF₄/PC based EDLCs remain linear and symmetrical, while the curves of TEMA-BF₄/PC become a little asymmetrical. Furthermore, with the increase of charging voltage, the charge–discharge curves of SBP-BF₄/PC based EDLCs being a little asymmetrical, while that of TEMA-BF₄/PC electrolyte based EDLCs become seriously asymmetrical. Meanwhile, the iR drop of SBP-BF₄/PC based EDLCs is much smaller than that of TEMA-BF₄/PC based EDLCs, indicating that the SBP-BF₄/PC electrolyte is stable without any sign of decomposition [19]. The above results show that the withstand voltage of SBP-BF₄/PC electrolyte is higher than that of TEMA-BF₄/PC

PC electrolyte, which is in agreement with the results of CV measurement (Fig. 6.).

The discharge capacitance and energy density of SBP-BF₄/PC and TEMA-BF₄/PC electrolytes based EDLCs are listed in Table 2. The discharge capacitance of SBP-BF₄/PC and TEMA-BF₄/PC electrolytes based EDLCs almost remain constant between the charging voltage ranges from 0–2.5 V to 0–3.0 V. The discharge capacitance of TEMA-BF₄/PC electrolytes based EDLCs begin to gradually decrease as charging voltage higher than 3.2 V, especially when charging voltage increase to 3.7 V. While the discharge capacitance of SBP-BF₄/PC electrolytes based EDLCs do not show obvious decrease as the charging voltage increase. So, the withstand voltage of SBP-BF₄/PC electrolytes is higher than that of TEMA-BF₄/PC, about 3.2 V and 3.0 V, respectively.

The energy density of SBP-BF₄/PC and TEMA-BF₄/PC electrolytes based EDLCs gradually increase with the charging voltage increase, and both achieve the highest values at the charging voltage of 3.5 V. However, the energy density of SBP-BF₄/PC electrolytes based

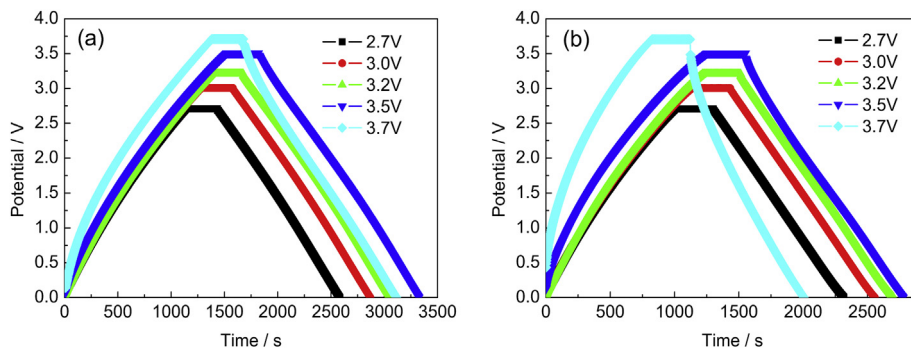


Fig. 8. Charge–discharge curves of the EDLCs with 1.5 M SBP-BF₄/PC and TEMA-BF₄/PC. The current density was 100 mA g⁻¹. (a) SBP-BF₄/PC (b) TEMA-BF₄/PC.

Table 2

The discharge capacitance and energy density of SBP-BF₄/PC and TEMA-BF₄/PC based EDLCs. The current density is 100 mA g⁻¹.

Sample	SBP-BF ₄ /PC		TEMA-BF ₄ /PC	
	Cg (F g ⁻¹)	Eg (Wh kg ⁻¹)	Cg (F g ⁻¹)	Eg (Wh kg ⁻¹)
2.5 V	120	26	108	24
2.7 V	118	30	105	27
3.0 V	120	38	105	33
3.2 V	121	43	104	37
3.5 V	122	52	103	44
3.7 V	117	56	75	36

Cg: the gravimetric discharge capacitance based on single electrode of the EDLCs.
Eg: the energy density based on the total mass of electrode active material.

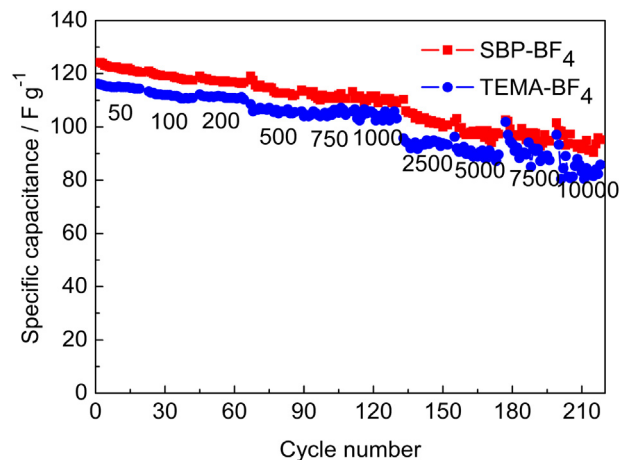


Fig. 9. The charge/discharge rates performance of EDLCs with 1.5 M SBP-BF₄/PC and TEMA-BF₄/PC as electrolyte obtained from galvanostatic charge/discharge tests carried out using a cell voltage of 2.7 V and current density range from 50 mA g⁻¹ to 10 A g⁻¹ at 298 K.

EDLCs is higher than that of TEMA-BF₄/PC electrolytes based EDLCs, about 52 Wh kg⁻¹ and 44 Wh kg⁻¹, respectively.

Fig. 9 gives the rate performance obtained from galvanostatic charge/discharge tests in the current density range from 50 mA g⁻¹ to 10 A g⁻¹. The discharge specific capacitance of EDLCs using two electrolyte systems decrease slowly in low discharge current density range, while the capacitance decrease rapidly from discharge current density of 2500 mA g⁻¹. When the discharge current density reach to 7500 mA g⁻¹, the specific discharge capacitance of

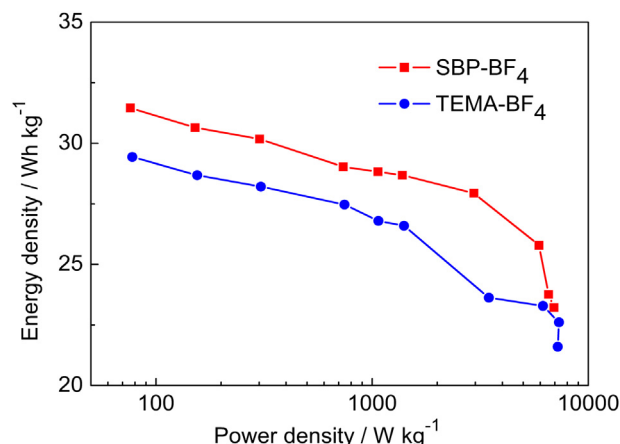


Fig. 10. Ragone plots for the EDLCs with 1.5 M SBP-BF₄/PC and TEMA-BF₄/PC.

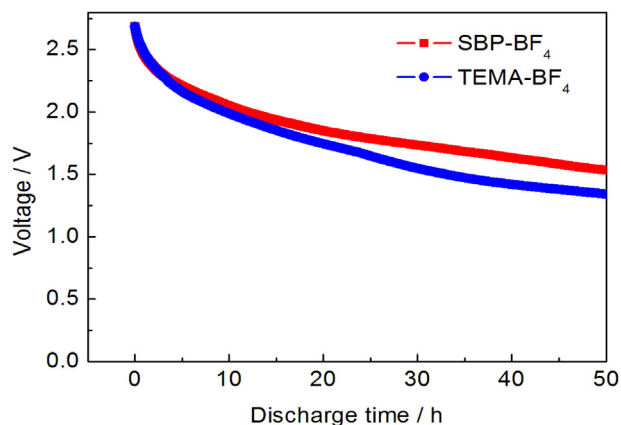


Fig. 11. Self-discharge curves of EDLCs with 1.5 M SBP-BF₄/PC and TEMA-BF₄/PC. Both capacitors were charged at 2.7 V for 3 h.

EDLCs become unstable suggesting that the stable electrode/electrolyte interface is destroyed especially for TEMA-BF₄/PC electrolyte. The charge/discharge rate performance of EDLCs using SBP-BF₄/PC electrolyte is better than that of TEMA-BF₄/PC especially at high discharge current density. The reason for the excellent rate performance of EDLCs using SBP-BF₄/PC electrolyte may be the smaller size, higher mobility, more rigid structure of the SBP ions compared to TEMA ions, higher electrical conductivity and lower viscosity of the SBP-BF₄/PC electrolyte compared to those of TEMA-BF₄/PC electrolyte in same concentration [8,24,25].

The specific energy and power relationship is shown in Fig. 10. The cell performance used SBP-BF₄/PC electrolyte is much better than that of TEMA-BF₄/PC. The energy density and power density of EDLCs using SBP-BF₄/PC electrolyte could reach to 31 Wh kg⁻¹ and 6938 W kg⁻¹, respectively.

The self-discharge curves indicating the voltage maintenance performance of capacitors are shown in Fig. 11. It can be seen that the voltage of SBP-BF₄/PC electrolytes based EDLCs decrease to 1.80 V after 24 h. The voltage maintenance ratio is 66.8%, while the voltage of TEMA-BF₄/PC electrolytes based EDLCs is comparatively lower about 1.67 V with the voltage maintenance ratio being 62.2%. After 48 h, the voltage of SBP-BF₄/PC electrolytes based EDLCs decrease to 1.55 V, which is still higher than that of TEMA-BF₄/PC with 1.36 V. The voltage maintenance of EDLCs using SBP-BF₄/PC and TEMA-BF₄/PC electrolytes are 57.6% and 50.4%, respectively. When applied voltage removed, the diffused layer ions absorbed on

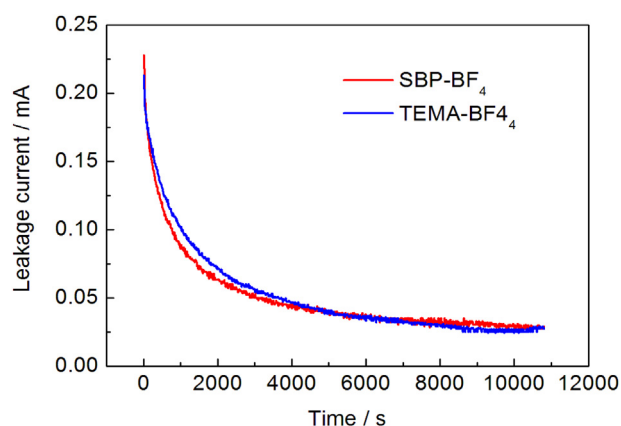


Fig. 12. The leakage current of EDLCs with 1.5 M SBP-BF₄/PC and TEMA-BF₄/PC. Both capacitors were charged at 2.7 V for 3 h.

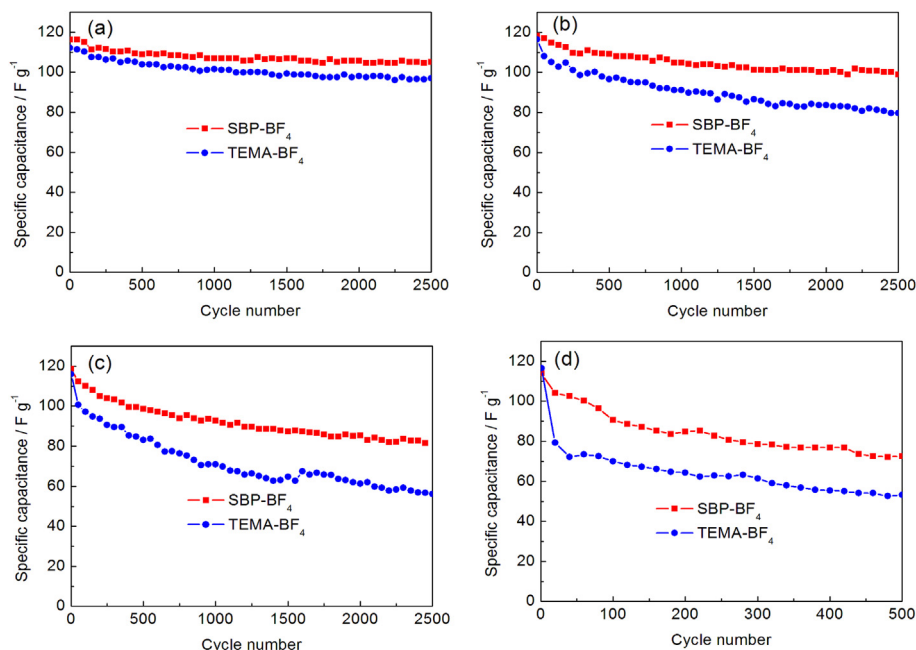


Fig. 13. The cycle life of EDLCs with 1.5 M SBP-BF₄/PC and TEMA-BF₄/PC as electrolyte obtained from galvanostatic charge/discharge tests carried out using current density of 500 mA g⁻¹. The cell working voltage is (a) 2.7 V (b) 3.0 V (c) 3.2 V (d) 3.5 V.

the interface go back to the solution rapidly. The potential drops rapidly in the first several hours. While the voltage of TEMA-BF₄/PC electrolytes based EDLCs declines faster than that of SBP-BF₄/PC electrolytes based EDLCs, which indicates the voltage maintenance of SBP-BF₄/PC electrolytes based EDLCs is better than that of TEMA-BF₄/PC electrolytes based EDLCs.

The leakage current of the SBP-BF₄/PC and TEMA-BF₄/PC are shown in Fig. 12. The current at 900 s is defined as the leakage current of EDLCs [34]. From the curves, the EDLCs based on SBP-BF₄/PC electrolytes has lower leakage current with 0.092 mA than the TEMA-BF₄/PC electrolytes based EDLCs with 0.107 mA. The SBP-BF₄/PC electrolytes based EDLCs exhibits a better leakage current character than TEMA-BF₄/PC electrolytes based EDLCs.

As expected, the SBP-BF₄/PC based capacitors have a better cycle life than that of TEMA-BF₄/PC based capacitors, as shown in Fig. 13. After 2500 cycles at the working voltage of 2.7 V, the specific capacitance of SBP-BF₄/PC and TEMA-BF₄/PC based capacitors can remain as high as 95 F g⁻¹ and 87 F g⁻¹, respectively. When the working voltage increase to 3.0 V, the specific capacitance of SBP-BF₄/PC and TEMA-BF₄/PC based capacitors can remain as high as 89 F g⁻¹ and 67 F g⁻¹ after 2500 cycles. However, the specific capacitance of SBP-BF₄/PC and TEMA-BF₄/PC based capacitors only have 72 F g⁻¹ and 46 F g⁻¹ after 2500 cycles at working voltage of 3.2 V. The specific capacitance of TEMA-BF₄/PC based capacitors decreases to 43 F g⁻¹ and remains only about 40% after 500 cycles compared to the initial discharge process, while the specific capacitance of SBP-BF₄/PC based capacitors decreases to 62 F g⁻¹ and remains about 60%. The SBP-BF₄/PC based capacitors exhibit much better cycle performance than TEMA-BF₄/PC based capacitors even at high working voltage.

4. Conclusion

This work demonstrated the superiority of the SBP-BF₄ salt as electrolyte for EDLCs to commercial electrolyte TEMA-BF₄ by CV, EIS and GCD methods. The electrical conductivity of SBP-BF₄/PC (17.0 mS cm⁻¹) is higher than that of TEMA-BF₄/PC (14.6 mS cm⁻¹).

The potential window of the two electrolytes was almost 5.2 V, which can provide wide-range application for supercapacitor, but the potential window of 1.5 M SBP-BF₄/PC electrolyte was more stable than that of TEMA-BF₄/PC electrolyte. The rectangular shape of the cyclic voltammetry at wide potential range suggested that the SBP-BF₄/PC electrolyte had good capacitor behavior and excellent upper voltage hold capability. The cell maintained good rate performance even at high discharge current density. The energy density and power density could reach to 31 kW kg⁻¹ and 6938 W kg⁻¹, respectively. The SBP-BF₄/PC based supercapacitors exhibit a better cycle life than TEMA-BF₄/PC based supercapacitors.

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